

## Characteristics of manganese nodules from sub-equatorial Indian Ocean between 4°30' S and 10° 30' S latitudes

R Banerjee & R Mukhopadhyay

National Institute of Oceanography, Dona Paula, Goa 403 004, India

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Manganese nodules from study area show rough surfaced nodules, occurring in SW part and abundant in greater water depths. They contain todorokite as the dominant mineral phase, have thicker oxide layer and are rich in Mn/Fe and Cu/Ni. In contrast smooth textured nodules, occurring in the NE part, show decrease in abundance with water depth, contain both todorokite and  $\delta$ -MnO<sub>2</sub>, record thin oxide layer and are poor in Mn/Fe and Cu/Ni. Possible diagenetic and hydrogenous influence on the formation and metal enrichment of rough and smooth textured nodules respectively have been discussed.

Physiographically, the Indian Ocean is the most complex of all world oceans<sup>1</sup>. This complexity in natural environment is reflected in the distribution, composition and origin of the Indian Ocean nodules<sup>2,3</sup>. Greater nodule coverage in the Indian Ocean is in the area south of the equator<sup>2,4</sup>. Local and regional variations in nodule chemistry, mineralogy and morphology from Central Indian Ocean Basin (CIOB) and adjacent areas as function of seafloor topography, microbathymetry and bottom sediment types are discussed<sup>3,5-9</sup>. However, studies on nodules from sub-equatorial Indian Ocean are scanty<sup>2</sup>. In the present work, an attempt has been made to understand the processes responsible for variability in morphology, geochemistry, mineralogy and growth rate of nodules from the sub-equatorial part of the CIOB.

### Materials and Methods

The study area lies between Chagos trench and Ninety east ridge, between lat. 4° 30' and 10° 30' S. Nodules were sampled by Peterson and free fall grabs during number of cruises in CIOB (1982-84). Water depth in the study area varied from 4500 m around 5°S to 5600 m around 10° S. In all, nodules from 20 different locations were studied. The sampling frequency was variable. At places the stations were at 1° to 1/2° interval and at places they were at 1/4° to 1/8° interval. The larger grid was chosen at the beginning of the survey, later depending on abundance and grade few areas were re-surveyed in a closed grid pattern. After collection, nodules were cleaned and their size (i.e. diameter), shape and surface texture were studied<sup>10</sup>.

Nodules were cut into 2 halves and their oxide layer thickness was measured. Then one half was preserved as reference and the bulk oxide layer of the other half was powdered to - 230 mesh and analysed by X-ray diffraction technique, with nickel filtered Cu K $\alpha$  target from 5° to 70° 2 $\theta$  and by atomic absorption spectrophotometer (AAS; Perkin-Elmer, PE-5000) to identify their major mineral phases and chemical compositions respectively. Relative abundance of todorokite (9.8A) and  $\delta$ -MnO<sub>2</sub> (2.41A) were estimated from their peak height ratios in the diffractogram<sup>11</sup>. Samples for AAS analyses were prepared through standard HF, HNO<sub>3</sub>, HClO<sub>4</sub> treatment and analysed in duplicate with 0.1 N HCl, along with USGS A-1 manganese nodule standard. The precision was  $\pm$  5%.

### Results and Discussion

Abundance of nodules show that areas having predominantly smooth nodules, exhibit greater abundance (9.32 kg.m<sup>-2</sup>) than those having rough surface nodules (7.36 kg.m<sup>-2</sup>). Towards higher latitudes abundance of smaller nodules (< 6 cm diam.) increases, while that of larger nodules (> 6 cm diam.) decreases. This trend of decreasing abundance with increase in size may result either from the winnowing mechanism and/or by selective burial<sup>12</sup>. These 2 processes may be responsible respectively for the variable abundance of smaller and larger nodules in the study area. The overall distribution of nodules in this region shows that they are predominantly small in size (2-4 cm diam.) and subspheroidal in shape. In general, the nodules show marked variations in their morphological

Table 1—Location, depth, morphology, chemistry, mineralogy, and growth rate of nodules

St.* No.	Position		Depth (m)	Surface texture	Concentration(%)					Ratio			Growth rate (mm.10 <sup>-6</sup> y)	Tod/ δ-MnO <sub>2</sub> †
	Lat	Long			Mn	Fe	Ni	Cu	Co	Cu/Ni	Mn/Fe			
1	7° 00'00"	83° 01'12"	4920	S	20.46	09.14	00.71	00.44	00.14	0.62	2.24	4.40	1.85	
2	6° 59'36"	84° 59'18"	4620	S	19.47	09.14	00.65	00.48	00.12	0.74	2.13	4.20	1.84	
3	7° 58'18"	84° 55'18"	4900	S	19.80	13.49	00.34	00.19	00.19	0.56	1.47	2.20	1.85	
4	7° 01'06"	88° 01'30"	5080	S	17.49	10.44	00.48	00.33	00.11	0.69	1.68	3.00	1.92	
5	8° 00'30"	78° 58'24"	5335	S	11.88	12.62	00.61	00.51	00.08	0.84	0.94	1.60	2.06	
6	9° 59'54"	74° 59'12"	5178	R	26.07	03.92	01.05	00.96	00.07	0.91	6.66	27.50	2.86	
7	9° 59'18"	74° 58'48"	5180	R	26.07	03.05	01.08	00.90	00.05	0.83	8.55	45.30	3.72	
8	5° 00'00"	75° 59'18"	4492	S	21.45	07.83	00.74	00.61	00.11	0.82	2.74	6.20	1.96	
9	8° 00'00"	75° 59'24"	5263	S	17.82	09.57	00.64	00.43	00.09	0.67	1.86	3.60	2.05	
10	9° 58'12"	75° 57'06"	5328	R	22.11	06.96	00.89	00.67	00.09	0.75	3.18	7.70	2.54	
11	8° 28'48"	81° 30'12"	5273	S	19.80	13.05	00.42	00.20	00.16	0.48	1.52	2.30	2.46	
12	8° 29'12"	81° 00'12"	5350	R	24.09	04.79	01.02	01.01	00.09	0.99	5.03	17.20	3.08	
13	7° 56'30"	81° 30'12"	5263	S	20.79	08.27	00.72	00.49	00.13	0.68	2.51	5.30	1.48	
14	9° 59'18"	75° 45'06"	5280	R	26.40	03.92	01.16	00.99	00.06	0.85	6.74	28.00	3.78	
15	9° 59'30"	76° 15'06"	5400	R	23.43	04.35	01.10	00.76	00.07	0.69	5.39	20.30	2.66	
16	9° 59'24"	76° 44'30"	5380	R	23.76	05.66	01.04	00.82	00.07	0.79	4.20	12.30	3.73	
17	9° 30'12"	75° 30'18"	5390	R	25.74	03.48	01.24	00.99	00.05	0.80	7.40	34.50	3.20	
18	9° 30'18"	75° 59'24"	5350	R	22.44	05.66	01.00	00.78	00.09	0.78	3.97	11.60	3.14	
19	9° 59'24"	76° 29'12"	5280	R	49.83	08.27	01.95	01.92	00.14	0.98	6.02	12.11	2.91	
20	9° 59'12"	78° 29'30"	5300	R	24.42	06.53	01.02	00.78	00.10	0.76	3.74	9.60	2.69	

S = smooth and R = rough

\*NE—1-5, 8, 9, 11-13  
SW—6, 7, 10, 14-20.

characters. With increase in depth towards SW part nodule size increases; shape and surface texture also changes respectively from subspheroidal to elongate and smooth to rough. The average oxide layer thickness of rough nodules is higher (0.78 cm) than that of smooth nodules (0.46 cm). Occurrence of smooth nodules at shallower depth and rough nodules at deeper part can be explained by their variable processes of growth, viz. hydrogenous and early diagenetic respectively<sup>13</sup>.

Chemical composition indicates considerable variation in major and minor elements concentration with respect to nodule morphology and water depth. (Table 1). The average Mn/Fe ratio shows higher values (5.4) for rough nodules of deeper area at the SW

part, than those of smooth nodules (1.9) from the shallower depth at the NE part. In general Co shows a negative correlation, while Ni and Cu show positive correlation with Mn ( $r=0.89$  and  $0.9$ ; Fig. 1). Nodules from higher latitudes of the area show these correlations more strongly than those from lower latitudes. Cu/Ni ratio markedly increases with the increase in Mn/Fe ratio (Fig. 2). A strong positive correlation ( $r=0.79$ ; Fig. 1) occurs between Co and Fe suggesting their association in the same phase. Similar variations in the nodule composition from different parts of CIOB and also from NW part of the sub-equatorial Indian Ocean have earlier been observed<sup>6,8,14</sup>.

The enhanced concentration of Mn, Ni and Cu in the nodules from the SW part of the study area (sts 6,7,10,14-20 in Table 1) is probably controlled diagenetically by the decomposition of organic matter within the bottom sediment, the quantity of which is again influenced by surface biological productivity<sup>15</sup>. In the present area of high surface biological productivity<sup>16</sup>, Cu and Ni ratio in the water column is expected to rise below lysocline on dissolution of dead orga-

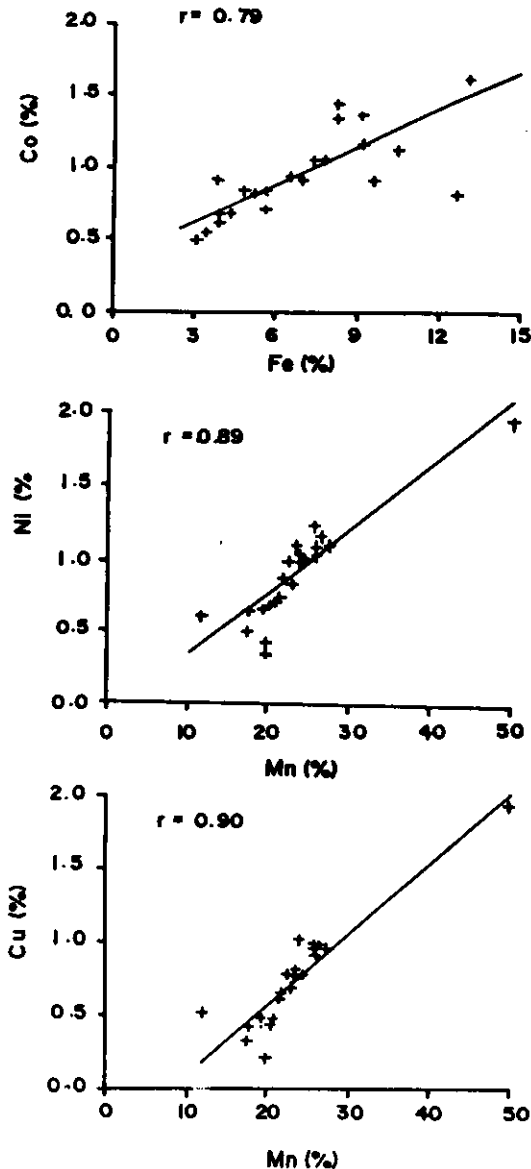


Fig. 1— Interelement relationships of the nodules

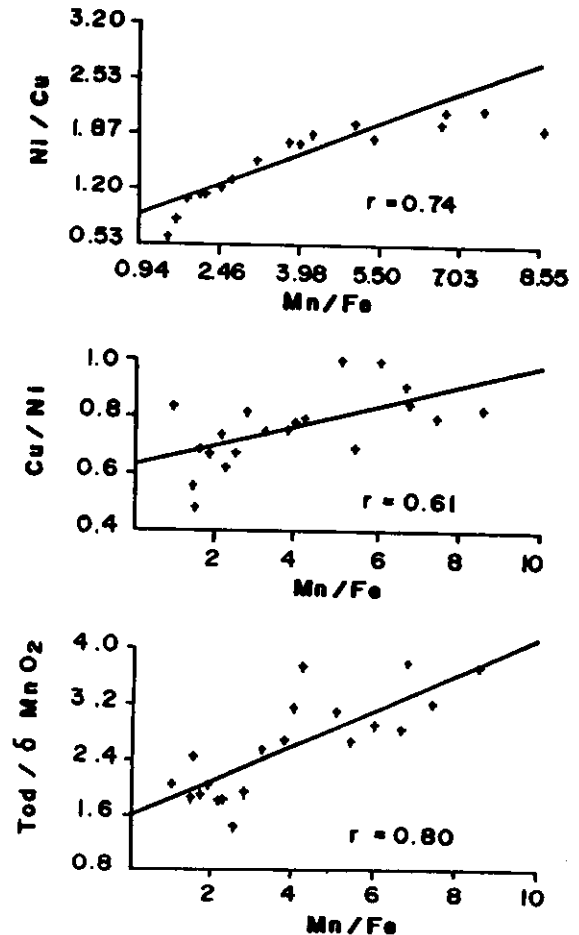


Fig. 2 Relationship between geochemistry and mineralogy of the nodules

nisms. Trace elements thus released in the water column also might have been possibly incorporated in the underlying nodules, through their intermediate layers of todorokite lattice<sup>17</sup>. In contrast nodules occurring in the shallower areas of NE part (sts 1-5, 8, 9, 11-13 in Table 1) are comparatively poor in Ni and Cu. This may be due to the partial dissolution of the sinking tests of dead organisms at a depth range between lysocline and carbonate compensation depth (CCD) and hence lack of trace metal supply to the water column and also in turn to the underlying nodules.

Concentration of Ni and Cu in these nodules show a positive relationship with Mn/Fe (Fig. 2). The concentration of Ni and Cu increases beyond the Mn/Fe ratio of 5, in contrast to the point of reversal advocated earlier<sup>18</sup>. Moreover, an apparent reverse trend in Ni + Cu concentration was observed after Mn/Fe ratio reaches 7 (Table 1). However, extensive studies on similar aspect on a number of nodules are required to arrive at a conclusion in this regard.

Mineralogical studies of these nodules by X-ray diffraction method show todorokite as the predominant manganese phase though  $\delta$ -MnO<sub>2</sub> is identified in many instances. Todorokite and  $\delta$ -MnO<sub>2</sub> peak height ratio (at 9.8 Å and 2.41 Å) increases with water depth (Table 1), Mn/Fe ratio (Fig. 2) and Ni + Cu content in the SW part of the area, indicate their early diagenetic growth<sup>11</sup>.

Preferential uptake of Ni and Cu by certain manganese oxide minerals is well exemplified here as nodules having higher concentration of Ni and Cu are found rich in todorokite (Fig. 2). On the other hand Ni and Cu contents are comparatively low in smooth surface  $\delta$ -MnO<sub>2</sub> rich nodules, as epitaxial intergrowths between iron hydroxides and manganese oxides offer limited sites for Ni and Cu uptake in disordered  $\delta$ -MnO<sub>2</sub> structure<sup>17</sup>. Todorokite rich nodules showing higher Mn/Fe ratios, rough surface textures and high trace metal concentration (Ni and Cu) are considered to be a product of early diagenesis<sup>3, 18</sup>.

Following Lyle's<sup>19</sup> equation, it is found that rough nodules having a predominant todorokite mineral phase, grow at a much faster rate (5.12 to 45.44 mm.10<sup>-6</sup>y), as observed by their thick oxide layers, than the smooth nodules (1.65 to 6.05 mm.10<sup>-6</sup>y; Table 1). This observation is in good agreement with earlier studies<sup>18, 20</sup> on nodule growth rate. The smooth surface being the product of hydrogenetic process shows low growth rate (< 7 mm.10<sup>-6</sup>y) while the rough surface being the product of early diagenetic process shows high growth rates (up to 45 mm.10<sup>-6</sup>y). Radiometrically determined growth rate of nodules

from different parts of the Indian Ocean<sup>21, 22</sup> however, are much less (1-8 mm.10<sup>-6</sup>y) than the growth rates reported here.

The chemical composition, mineralogy and accretion rate of the rough and smooth nodules obtained from diagenetic and hydrogenous conditions of the SW and NE areas respectively are different in comparison to nodules occurring at similar conditions in other parts of the CIOB<sup>2, 6, 14</sup>. This reflects diagenetic influence for majority of these presently studied nodules at variance with the earlier observations<sup>14</sup> made on the nodules collected from equatorial CIOB. Ore and scanning electron microscopic studies of these nodules also reveal their diagenetic growth (unpublished). Further, a complex source of metal enrichment in the smooth nodules occurring at shallower depths in the NE part is envisaged from present observations. Significant mixing and lateral displacement of sediments by Antarctic bottom water have been observed in the Indian Ocean<sup>23</sup>. Similar to the observations made in equatorial Pacific<sup>11</sup>, in the present study area, transportation of diagenetically rich trace metals by bottom water from adjacent areas to the present site, might have played an important role as additional source for higher trace element concentrations in the smooth nodules.

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